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(57) Abstract

The inventive soldering compositions all contain a tin-silver-copper base. To this base are added varying combinations of indium, antimony, zinc and/or bismuth to form soldering compositions having the desirable properties described herein. Also disclosed are methods of soldering employing the compositions.

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SOLDERING COMPOSITION

The invention is directed to soldering alloys that are non-toxic, exhibit low melting temperatures, behave well in normal soldering applications such as, for example, hand soldering, wave soldering or paste reflow soldering, and impart useful long-term properties to the connections made with them.

Tin has a melting temperature of about 232°C, and is the primary ingredient of the inventive compositions. Tin readily wets a large number of other metals and forms a eutectic with many of these alloys. (A eutectic is a low melting temperature alloy of specific composition that changes from liquid to two or more solid phases at a precise single temperature rather than solidifying over a temperature span often referred to as a "pasty range".) While tin can be an adequate solder when used alone, it suffers from two significant drawbacks. First, its melting temperature of 232°C is too high for many soldering applications, including routine electronic circuit assembly. The addition of other alloying ingredients can lower the melting temperature. Second, tin forms an allotropic, beta phase at reduced temperatures. This phase is non-metallic and has very low strength. The presence of certain alloying ingredients can inhibit the formation of this phase.

In formulating the inventive compositions, the choice of which chemical elements should be added to tin and in what amounts was made with several factors in mind. First, low toxicity was required of all alloying elements used in the compositions. For this reason, lead, which is a standard though toxic element used for these purposes, is not used in any of the inventive compositions. Second, a substantial reduction in the melting temperature of 232°C was required. Third, high wettability of the composition on common substrate surfaces, such as copper, was important. Fourth, good melting behavior of the composition was required. For instance, it is often beneficial for a solder to exhibit a limited temperature range pasty range, thereby resembling a eutectic material. Fifth, low cost and availability of alloying elements was desirable. Sixth, a low chemical reactivity of the molten solder alloys with air was desirable. Seventh, a low corrosion rate was important. Finally, good mechanical properties of the alloy compositions were required.

The binary alloy which forms the foundation for the inventive compositions is the well known tin-silver eutectic 96.5Sn-3.5Ag with a melting temperature of about 221°C. All compositions are given in percent by weight unless otherwise indicated. Copper is then added to this binary alloy to produce a nearly eutectic tin-silver-copper ternary alloy which is one of the

inventive compositions and is the base for the remaining inventive compositions. A preferred composition of this ternary alloy is 95.8Sn-3.5Ag-0.67Cu with a solidus temperature of about 213°C and a liquidus temperature of about 218°C.

Many solder compositions are known, but most have one or more poor properties. For example, alloys containing significant fractions of antimony have poor wetting characteristics and melting temperatures that are too high for many applications. Zinc-tin eutectic solder has a favorable melting temperature of 199°C, but the zinc in the molten alloy oxidizes rapidly when contacted with air. Alloys having relatively low silver fractions have broad pasty ranges which, while suitable for many plumbing applications, are not useful in electronics applications, where a eutectic or nearly eutectic alloy is favorable. Tin-based solders having significant bismuth contents generally have poor fatigue characteristics (relative to the standard tin-lead eutectic solder). Even the tin-lead eutectic solder has drawbacks apart from its toxicity. For example, the fatigue behavior of this alloy is inferior to most of the present non-bismuth containing inventive compositions.

The inventive compositions have unusually good combinations of the most important solder properties -- namely, wettability, fatigue life, cost and corrosion resistance. They also have demonstrated excellent strength (relative to the tin-lead eutectic solder) and high resistance to electrochemical migration.

SUMMARY OF THE INVENTION

A soldering composition comprising by weight about 3.1-3.5% silver, 0.5-2.7% copper and the balance tin, having a preferred composition of about 3.5% silver, 0.67% copper and 95.8% tin. A further soldering composition comprising by weight about 3.7-4.6% silver, 1.0-1.6% copper and the balance tin, having a preferred composition of about 4.5% silver, 1.5% copper and 94.0% tin. A further soldering composition comprising by weight about 3.1-6.5% silver, 0.25-0.8% copper and the balance tin, having a preferred composition of about 5.0% silver, 0.7% copper and 94.3% tin. A further soldering composition comprising by weight about 1.5-7.0% silver, 0.4-1.4% copper, 0.5-6.0% indium and the balance tin, having a preferred composition of about 3.3% silver, 0.67% copper, 4.1% indium and 91.9% tin. A further soldering composition comprising by weight about 0.1-6.0% silver, 0.1-0.4% copper, 0.1-2.0% antimony and the balance tin, having a preferred composition of about 5.0% silver, 0.4% copper, 0.3% antimony and 94.3% tin. A further soldering composition comprising by weight about 3.0-5.2% silver,

0.4-2.7% copper, 0.4-2.6% zinc and the balance tin, having a preferred composition of about 3.6% silver, 0.67% copper, 1.1% zinc and 94.6% tin. A further soldering composition comprising by weight about 1.4-7.1% silver, 0.5-1.3% copper, 0.2-9.0% indium, 0.4-2.7% antimony and the balance tin, having a preferred composition of about 3.3% silver, 0.66% copper, 4.2% indium, 1.3% antimony and 90.5% tin. A further soldering composition comprising by weight about 0.1-10.0% silver, 0.1-3.0% copper, 0.07-20.0% indium, 0.05-9.0% zinc and the balance tin, having a preferred composition of about 3.3% silver, 0.66% copper, 4.2% indium, 1.3% zinc and 90.5% tin. A further soldering composition comprising by weight about 1.5-4.5% silver, 0.3-1.4% copper, 0.1-10.0% indium, 0.01-0.5% antimony, 0.01-3.0% zinc and the balance tin, having a preferred composition of about 3.5% silver, 0.69% copper, 0.44% indium, 0.45% antimony, 0.11% zinc and 94.8% tin. A further soldering composition comprising by weight about 0.2-7.4% silver, 0.2-1.4% copper, 0.02-8.0% indium, 0.02-10.0% bismuth and the balance tin, having a preferred composition of about 3.5% silver, 0.69% copper, 2.2% indium, 4.5% bismuth and 89.1% tin. A further soldering composition comprising by weight about 3.1-7.4% silver, 0.2-1.4% copper, 0.02-2.5% antimony, 0.02-2.4% zinc and the balance tin, having a preferred composition of about 3.5% silver, 0.69% copper, 1.4% antimony, 1.1% zinc and 93.3% tin.

Also an aspect of the invention is a method for soldering comprising the step of employing a solder composition of the invention.

DETAILED DESCRIPTION

A table of the properties of the preferred compositions of the inventive solders, as well as the standard tin-lead eutectic solder, follows:

Alloy	Melting Range	Solderability on Cu	Fatigue	Corrosion
		(1)		
95.8Sn-3.5Ag -0.67Cu	213°C solidus ~218°C liquidus	Excellent. Very similar to standard alloy (12) below for the same superheating.	Best of alloys shown.	Very Good.

		(2)		
94.0Sn-4.5Ag-1.5Cu	214°C solidus ~215°C liquidus	Excellent. Very similar to standard alloy (12) below for the same superheating.	With alloy (1), best of all alloys shown.	Very good.
		(3)		
94.3Sn-5.0Ag-0.7Cu	214°C solidus ~216°C liquidus	Near excellent.	Very good.	Very good.
		(4)		
91.9Sn-3.3Ag-0.67Cu-4.1In	211°C solidus ~217°C liquidus	Good but poorer than alloys (9) and (10) below.	Very good.	Good to very good.
		(5)		
94.3Sn-5.0Ag-0.4Cu-0.3Sb	214°C solidus ~224°C liquidus	Very good.	Very good.	Very good.
		(6)		
94.6Sn-3.6Ag-0.67Cu-1.1Zn	214°C solidus ~218°C liquidus	Slightly worse than alloy (4) above.	Good.	Good.
		(7)		
90.5Sn-3.3Ag-0.66Cu-4.2In-1.3Sb	198°C solidus ~215°C liquidus	Very good. Between alloys (4) and (8).	Good.	Good to very good.
		(8)		
90.5Sn-3.3Ag-0.66Cu-4.2In-1.3Zn	190°C solidus ~215°C liquidus	Nearly as good as alloy (9) below.	Medium.	Fair.

		(9)		
94.8Sn-3.5Ag -0.69Cu-0.44In -0.45Sb-0.11Zn	214°C solidus ~220°C liquidus	Excellent. Best of all alloys shown.	Very good.	Good to very good.
		(10)		
89.1Sn-3.5Ag -0.69Cu-2.2In -4.5Bi	142°C solidus ~204°C liquidus	Fair to good.	Fair to poor. About same asstandard alloy (12) below.	Fair.
		(11)		
93.3Sn-3.5Ag -0.69Cu-1.4Sb -1.1Zn	213°C solidus ~220°C liquidus	Slightly worse than alloy (42) above.	Excellent.	Good.
		(12)		
Standard 63Sn-37Pb	183°C eutectic	Excellent.	Fair to poor	Fair to poor.

Each of the properties described in the above table was measured using conventional means. Melting temperature was measured using a Dupont Model 2100 thermogravimetric analyzer containing a differential scanning calorimetry (or "DSC") cell commercially available from Thermal Analysis Instruments of New Castle, Delaware. The solder sample to be measured was placed in one of two locations within the DSC cell. A dummy specimen was placed in the other locations in the DSC cell. The temperature of the apparatus was then raised at a specified rate, and the difference in thermocouple voltages from the two specimens was monitored. The melting process was detected through changes in this voltage signal. For example, the melting point of pure elements and eutectic alloys can be detected by a sharp drop in this signal.

Solderability was measured using a conventional wetting balance method. Summarizing this method, liquid flux was applied to a standard test strip (of copper, in this case). The test strip was then fastened to a Multicore Universal Solderability Test (or "MUST") device commercially available from

Multicore Solders of Richardson, Texas. A molten bath of the solder to be tested was then placed in a solder pot contained in the device and brought to a predetermined temperature. An automatic test cycle of the device then began by raising the solder pot until electrical contact was made with the test strip, at which point the pot was raised an additional predetermined amount. The apparent weight of the test strip was then measured as the solder lifted and then wet up on the test strip. The rate of wetting and the maximum weight of the solder applied to the strip indicate solderability.

Fatigue was measured using a test electronic circuit board containing multiple leads. The solder to be measured was applied to the board to form one or more continuous circuits (referred to as "daisy chains") connecting the leads. As strain is applied to the board, the solder will accumulate fatigue until the circuit is broken. Different methods used to apply strain to the board involved an isothermal bending test, in which the board was bent in different directions at high speed (approximately two cycles per minute) and uniform temperature, and a thermal cycling test, in which the board was more slowly cycled through hot and cold temperatures (approximately 80° C to -30° C) repeatedly.

Corrosion was tested using a conventional process in which the solder sample to be measured was formed into an electrode. Both this electrode and a standard calomel electrode were placed into a 0.04% ammonium chloride solution, and the potential between these two electrodes was then measured. A more positive potential for the electrode being tested indicates a more corrosion resistant solder sample.

Referring to the table shown above, alloys (1)-(3) generally contain a higher silver content than most existing tin-silver-based solders. This somewhat higher silver content results in a more nearly eutectic solder, desirable in electronic applications.

The addition of indium in alloy (4) improves the wetting behavior and lowers the melting temperature, with little impairment of fatigue life or corrosion resistance. The addition of copper also lowers the melting temperature and helps strengthen the alloy.

The antimony addition to alloy (5) suppresses the undesirable beta tin phase referred to above.

A higher silver content and the elimination of antimony and nickel distinguish alloy (6) from existing solders. The removal of antimony softens the alloy but not to a significant degree, while the removal of nickel results in a

better behaved alloy that is easier to manufacture. The higher silver content, as mentioned above, results in a more nearly eutectic alloy.

The addition of indium in alloy (7) reduces the melting temperature and, because the indium and antimony levels are relatively low, improves the fatigue characteristics.

The combination of indium and zinc in alloy (8) lowers the melting temperature. Also, the addition of zinc, in place of indium, lowers the cost of the alloy.

The addition of indium in alloy (9) improves the wetting behavior and, with the antimony and zinc additions, all in limited amounts, improves fatigue life.

The addition of bismuth and indium together in alloy (10) reduces the melting temperature.

The higher silver content of alloy (11) distinguishes it from existing solders. As stated above, this higher silver content results in a more nearly eutectic solder that is desirable in electronic applications.

Each of the inventive compositions can be used in all the major modes of usage for electronic soldering (for example, hand soldering, wave soldering and paste reflow soldering). Each of the inventive compositions can be made easily by melting pure tin and adding the remaining alloying elements. For quantities of up to about one kilogram, this can be done in a ceramic crucible or in borosilicate glass labware. The resulting compositions can be used as melted for wave soldering. For use in hand soldering, the resulting compositions generally are extruded to form a wire which can contain flux, if desired.

Conventional reflow soldering requires the placement of the solder components into prints of solder paste which are then heated, usually in a belt oven. For this use, the solder generally is made into a powder and blended with a suitable flux and other vehicle materials. Solder powders can be made using a variety of known techniques. One such technique involves atomizing molten solder with a burst of pressurized nitrogen, collecting the powders, separating into the desired size fraction, remelting the other size fractions, and repeating the process.

What is claimed is:

1. A soldering composition comprising by weight percent:
   a) from about 3.1 to about 3.5% silver;
   b) from about 0.5 to about 2.7% copper; and
   c) from about 93.8 - 96.4% tin.

2. The composition of claim 1 comprising by weight percent:
   a) about 3.5% silver;
   b) about 0.67% copper; and
   c) about 95.83% tin.

3. A soldering composition comprising by weight percent:
   a) from about 3.7 to about 4.6% silver;
   b) from about 1.0 to about 1.6% copper; and
   c) from about 93.8 to about 95.3 tin.

4. The composition of claim 3 comprising by weight percent:
   a) about 4.5% silver;
   b) about 1.5% copper; and
   c) about 94.0% tin.

5. A soldering composition comprising by weight percent:
   a) from about 3.1 to about 6.5% silver;
   b) from about 0.25 to about 0.8% copper; and
   c) from about 92.7 to about 96.65% tin.

6. The composition of claim 5 comprising by weight percent:
   a) about 5.0% silver;
   b) about 0.7% copper; and
   c) about 94.3% tin.

7. A soldering composition comprising by weight percent:
   a) from about 1.5 to about 7.0% silver;
   b) from about 0.4 to about 1.4% copper;
   c) from about 0.5 to about 6.0% indium; and
   d) from about 85.6 to about 97.6% tin.

8. The composition of claim 7 comprising by weight percent:
   a) about 3.3% silver;
   b) about 0.67% copper;
   c) about 4.1% indium; and
   d) about 91.93% tin.

9. A soldering composition comprising by weight percent:
   a) from about 0.1 to about 6.0% silver;
   b) from about 0.1 to about 0.4% copper;
   c) from about 0.1 to about 2.0% antimony; and
   d) from about 91.6 to about 99.7% tin.

10. The composition of claim 9 comprising by weight percent:
   a) about 5.0% silver;
   b) about 0.4% copper;
   c) about 0.3% antimony; and
   d) about 94.3% tin.

11. A soldering composition comprising by weight percent:
   a) from about 3.0 to about 5.2% silver;
   b) from about 0.4 to about 2.7% copper;
   c) from about 0.4 to about 2.6% zinc; and
   d) from about 89.5 to about 96.2% tin.

12. The composition of claim 11 comprising by weight percent:
   a) about 3.6% silver;
   b) about 0.67% copper;
   c) about 1.1% zinc; and
   d) about 94.6% tin.

13. A soldering composition comprising by weight percent:
   a) from about 1.4 to about 7.1% silver;
   b) from about 0.5 to about 1.3% copper;
   c) from about 0.2 to about 9.0% indium;
   d) from about 0.4 to about 2.7% antimony; and
   e) about 79.9 to about 97.5% tin.

14. The composition of claim 13 comprising by weight percent:

a) about 3.3% silver;
b) about 0.66% copper;
c) about 4.2% indium;
d) about 1.3% antimony; and
e) about 90.46% tin.

15. A soldering composition comprising by weight percent:
a) from about 0.1 to about 10.0% silver;
b) from about 0.1 to about 3.0% copper;
c) from about 0.07 to about 20.0% indium;
d) from about 0.05 to about 9.0% zinc; and
e) from about 58.0 to about 99.6% tin.

16. The composition of claim 15 comprising by weight percent:
a) about 3.3% silver;
b) about 0.66% copper;
c) about 4.2% indium;
d) about 1.3% zinc; and
e) about 90.54% tin.

17. A soldering composition comprising by weight percent:
a) from about 1.5 to about 4.5% silver;
b) from about 0.3 to about 1.4% copper;
c) from about 0.1 to about 10.0% indium;
d) from about 0.01 to about 0.5% antimony;
e) from about 0.01 to about 3.0% zinc;
f) from about 80.6 to about 98.08% tin.

18. The composition of claim 17 comprising by weight percent:
a) about 3.5% silver;
b) about 0.69% copper;
c) about 0.44% indium;
d) about 0.45% antimony;
e) about 0.11% zinc; and
f) about 94.8% tin.

19. A soldering composition comprising by weight percent:
 a) from about 0.2 to about 7.4% silver;
 b) from about 0.2 to about 1.4% copper;
 c) from about 0.02 to about 8.0% indium;
 d) from about 0.02 to about 10.0% bismuth; and
 e) from about 73.2 to about 99.56% tin.

20. The composition of claim 19 comprising by weight percent:
 a) about 3.5% silver;
 b) about 0.69% copper;
 c) about 2.2% indium;
 d) about 4.5% bismuth; and
 e) about 89.1% tin.

21. A soldering composition comprising by weight percent:
 a) from about 3.1 to about 7.4% silver;
 b) from about 0.2 to about 1.4% copper;
 c) from about 0.02 to about 2.5% antimony;
 d) from about 0.02 to about 2.4% zinc; and
 e) from about 86.3 to about 96.66% tin.

22. The composition of claim 21 comprising by weight percent:
 a) about 3.5% silver;
 b) about 0.69% copper;
 c) about 1.4% antimony;
 d) about 1.1% zinc; and
 e) about 93.3% tin.

23. A method of soldering comprising the step of employing a solder having a composition by weight percent chosen from the group consisting of: (a) from about 3.1 to about 3.5% silver, from about 0.5 to about 2.7% copper, and from about 93.8 - 96.4% tin; (b) from about 3.7 to about 4.6% silver, from about 1.0 to about 1.6% copper, and from about 93.8 to about 95.3 tin; (c) from about 3.1 to about 6.5% silver, from about 0.25 to about 0.8% copper, and from about 92.7 to about 96.65% tin; (d) from about 1.5 to about 7.0% silver, from about 0.4 to about 1.4% copper, from about 0.5 to about 6.0% indium, and from about 85.6 to about 97.6% tin; (e) from about 0.1 to about 6.0% silver, from about 0.1 to about 0.4% copper, from about 0.1 to about 2.0% antimony,

and about 91.6 to about 99.7% tin; (f) from about 3.0 to about 5.2% silver, from about 0.4 to about 2.7% copper, from about 0.4 to about 2.6% zinc, and from about 89.5 to about 96.2% tin; (g) from about 1.4 to about 7.1% silver, from about 0.5 to about 1.3% copper, from about 0.2 to about 9.0% indium, from about 0.4 to about 2.7% antimony, and from about 79.9 to about 97.5% tin; (h) from about 0.1 to about 10.0% silver, from about 0.1 to about 3.0% copper, from about 0.07 to about 20.0% indium, from about 0.05 to about 9.0% zinc, and from about 58.0 to about 99.6% tin; (i) from about 1.5 to about 4.5% silver, from about 0.3 to about 1.4% copper, from about 0.1 to about 10.0% indium, from about 0.01 to about 0.5% antimony, from about 0.01 to about 3.0% zinc, from about 80.6 to about 98.08% tin; (j) from about 0.2 to about 7.4% silver, from about 0.2 to about 1.4% copper, from about 0.02 to about 8.0% indium, from about 0.02 to about 10.0% bismuth, and from about 73.2 to about 99.56% tin; and (k) from about 3.1 to about 7.4% silver, from about 0.2 to about 1.4% copper, from about 0.02 to about 2.5% antimony, from about 0.02 to about 2.4% zinc, and from about 86.3 to about 96.66% tin.

24. The method claim of 23 wherein the composition by weight percent is chosen from the group consisting of: (l) about 3.5% silver, about 0.67% copper, and about 95.83% tin; (m) about 4.5% silver, about 1.5% copper, and about 94.0% tin; (n) about 5.0% silver, about 0.7% copper, and about 94.3% tin; (o) about 3.3% silver, about 0.67% copper, about 4.1% indium, and about 91.93% tin; (p) about 5.0% silver, about 0.4% copper, about 0.3% antimony, and about 94.3% tin; (q) about 3.6% silver, about 0.67% copper, about 1.1% zinc, and about 94.6% tin; (r) about 3.3% silver, about 0.66% copper, about 4.2% indium, about 1.3% antimony, and about 90.46% tin; (s) about 3.3% silver, about 0.66% copper, about 4.2% indium, about 1.3% zinc, and about 90.54% tin; (t) about 3.5% silver, about 0.69% copper, about 0.44% indium, about 0.45% antimony, about 0.11% zinc, and about 94.8% tin; (u) about 3.5% silver, about 0.69% copper, about 2.2% indium, about 4.5% bismuth, and about 89.1% tin; and (v) about 3.5% silver, about 0.69% copper, about 1.4% antimony, about 1.1% zinc, and about 93.3% tin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13720

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : C22C 13/00, 13/02
US CL : 420/560, 561
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 420/560, 561

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAS ONLINE
search terms: Ag, Cu, In, Sb, Zn, Bi, Sn

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,643,875 (MIZUHARA) 17 February 1987, abstract.	1-6, 23-24
X	US,A, 4,695,428 (BALLENTINE ET AL) 22 September 1987, abstract.	1-6, 9-12, 21-24
X --- Y	US,A, 4,797,328 (BOEHM ET AL) 10 January 1989, abstract and col. 2, line 17.	1-8, 23-24 --- 9, 10, 13--22
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Date of the actual completion of the international search	Date of mailing of the international search report
25 SEPTEMBER 1996	11 OCT 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13720

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US,A, 1,437,641 (FERRIERE ET AL) 05 December 1922, whole document.	1-6, 11, 12, 23-24 ---------------- 7-10, 13-22
Y	US,A, 5,393,489 (GONYA ET AL) 28 February 1995, abstract.	9, 10, 13, 14, 17, 18, 21, 22
X	Database WPIDS, AN 93-112315, JP 05-050286 A (MATSUSHITA ELEC IND CO LTD), abstract.	1-6, 23-24
X	DE 2054542 (SIEMENS AG.) 10 May 1972 (10.05.72), abstract.	1-6, 23-24

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